

Ketone Excited State Lifetimes

Measured by Deep UV Ultrafast Photoionization Spectroscopy

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ABSTRACT

Ultrafast photoionization spectroscopy has been used to measure excited state lifetimes for several ketones excited near 193 nm. The decay times for aliphatic ketones are between 2 and 9 ps, which are consistent with 3s Rydberg state predissociation and are similar to what has been observed previously for acetone. The lifetime of cyclic ketones are found to be somewhat longer than for acyclic ones, which is attributed to predissociation promoted by internal rotation for the latter. The aromatic ketone acetophenone dissociates more quickly and this is attributed to rapid intersystem crossing and/or interaction with a valence state that lies in this spectral region as a result of delocalization.

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1. Introduction

In photochemistry and particularly for molecules undergoing multiple dissociation, it is relevant to consider how the initially excited state dissociation and its lifetime influence the subsequent dynamics. The excited state lifetime is relevant not only to fundamental photodissociation dynamics for isolated molecules but also to considering the prospects for optical control and how the dynamics may be altered in condensed phases. Rapid primary dissociation, such as for direct dissociation, is expected to favor impulsive product energy partitioning, while a longer, predissociative process may provide the time for energy redistribution associated with a more statistical distribution. Product studies are more prevalent than direct time-resolved studies of photodissociation and there are very few instances in which both types of investigations have been carried out for a particular system. Therefore, much remains to be learned about the connection between excited state lifetimes and product energy distributions and how their effects on any secondary dissociation dynamics.

In recent femtosecond photoionization studies in our laboratory we have investigated the photodissociation dynamics of acetone,^{1,2} acetyl cyanide and acetic acid³ for excitation near 193 nm. All of these species produce acetyl radical as an intermediate that undergoes secondary dissociation. For acetone, the excitation populates the 3s Rydberg state which has a 4.7 ps lifetime (13 ps for d6).^{1,2} For the other two molecules, the ionization potentials, and as a result the Rydberg states, are at significantly higher energy and the states accessed for excitation near 193 nm are valence states which were found to have very short lifetimes.³ Product energy distributions for these molecules have been reported at this wavelength,⁴⁻⁷ and these provide a basis for comparing our measured acetyl secondary dissociation times with those based on a statistical, RRKM model. It is interesting that the acetyl intermediate decay dynamics for acetyl cyanide and acetic acid were consistent with an RRKM model whereas acetyl from acetone was found to be non-RRKM in nature. Therefore, for these molecules the primary dissociation dynamics correlates if not influences the nature of the intermediate acetyl radical decay.

In the present work we have extended our mass-resolved femtosecond photoionization studies

to measure excited state lifetimes for several ketones, including methylethyl ketone, diethyl ketone, methylisobutyl ketone, 4-methylcyclohexanone, cyclopentanone, and acetophenone. The results indicate that lifetimes for the aliphatic ketones are similar to those for acetone while acetophenone exhibits a much shorter lifetime. This can be explained in terms of the delocalized electronic structure for the aromatic ketone.

2. Experimental

Mass-resolved ultrafast photoionization measurements of the excited state lifetimes were performed using an apparatus that has been previously described.¹ Very briefly, it consists of a Ti:Sapphire regeneratively amplified laser system for generating ~120 fs, 0.5 mJ pulses near 780 nm at a 3 kHz repetition rate. The deep UV pump (195 nm) and near UV (260) or blue (390nm) probe pulses are generated by three successive stages of nonlinear mixing using BBO. The instrumental time resolution is determined to be ~350 fs as determined by photoionization signals measured for rapidly dissociating gases, such as dichloroethylene. Photoions are mass resolved using a quadrupole mass spectrometer and the room temperature sample gases are slowly flowed at pressures $\sim 1 \times 10^{-4}$ Torr. Static spectra were measured in a 10 cm pathlength cell for pressures between 0.5 and 3 Torr using a conventional UV/vis spectrometer with a 0.5 nm slit width.

3. Results and Discussion

Normalized static absorption spectra in the region near the excitation wavelength (190-204 nm) are shown in Fig. 1 for several of the ketones investigated. The spectrum for acetophenone is broad and featureless (and decreases with wavelength) in this region. Acetophenone spectra for $\lambda > 200$ nm can be found in Calvert and Pitts⁸ and for longer wavelengths, the first three electronic transitions in Berger and Steel.⁹

Photoionization curves for excitation near 193 nm and detection of the parent photoions are

shown in Fig.2 for the ketones investigated. The excited state lifetimes determined by fitting to a single exponential decay are provided in Table I. All the molecules investigated, except for acetophenone, are saturated, aliphatic ketones. They exhibit primary dissociation times between 2 and 9 ps, similar to what we observed previously for predissociation of the 3s state of acetone for the which the lifetime is 4.7 ps.¹ In contrast, the aromatic ketone, acetophenone, exhibits a rapid, instrument-limited decay time.

The 3s Rydberg state that is populated for excitation of acetone near 193 nm is also the initially excited state for the other aliphatic ketones. The energy of a Rydberg state is given by $E_{n,*} = IP - R/(n - *)^2$, where IP is the ionization potential, * is the quantum defect (* = 1 for s, l=0), and R is the Rydberg constant (13.595 eV). The ionization potentials for the ketones investigated here (9.16-9.52 eV)¹⁰ are similar to acetone (9.70 eV),¹⁰ so that the energy of their 3s Rydberg states (5.76-6.12 eV, corresponding to transition wavelengths of 202-215 nm) are also expected to lie at nearly the same energy as for acetone so that these Rydberg states are the ones populated for excitation near 193 nm. The 2-9 ps ketone excited state lifetimes listed in Table I are therefore ascribed to predissociation of 3s Rydberg states.

Although the excited state lifetimes measured span a fairly narrow range of <10 ps, there is a trend between the molecular structure and the lifetimes. The cyclic ketone predissociation times (4.1-8.9 ps) is somewhat longer than for those with straight chains (1.9-4.1 ps, or extending to 4.7 ps if acetone is included). There is also a correlation in the measured absorption spectra shown in Fig. 1. The vibronic bands in the spectra are clearly narrower for the cyclic ketones. The more diffuse spectra for the straight chain ketones cannot be due to lifetime broadening since it is <3 cm⁻¹ which is much less than the resolution (0.5 nm. 125 cm⁻¹) at which the spectra were measured. We postulate that the broadening is due to internal rotation in the straight chain ketones. This also suggests that the faster predissociation for these may also be due to predissociation promoted by internal rotation. We previously suggested that the 3s Rydberg state predissociation of acetone may be promoted or mediated by internal rotation to explain the large isotope effect of the primary dissociation rate. For the aliphatic ketones investigated here, the primary dissociation dynamics appears to be qualitatively

similar to one another and to acetone. The predissociation-mediated lifetime is considerably longer than what has been calculated for the excited state based on an RRKM dissociation model.¹¹

Acetophenone, on the other hand, exhibits a rapid excited state decay. It is the only aromatic ketone studied and it is subject to electron delocalization. It appears that the excited state rapidly decays due to either predissociation or intersystem crossing. The former could be due to the presence of a valence state that is either directly excited at 193 nm and accounts for the short lifetime or that accelerates the predissociation rate of the Rydberg state compared to that of the aliphatic ketones. Alternatively, the mechanism could be similar to what has been observed by Warren and Bernstein¹² for the S_2 state (near 270 nm), for which the lifetime was inferred to be 260 fs based on the phosphorescence-detected photoexcitation linewidth (for the 0^0 band). In this case intersystem crossing was indicated by the long (540 ns) emission lifetime. The ionization potential of acetophenone (9.28 eV) is similar to the other ketones so that the 3s Rydberg should also be near 6 eV. However, the electronic structure of acetophenone is altered compared to the aliphatic ketones which is evident from the reported near UV electronic spectra. The aliphatic ketones have only one optically active band at an energy lower than the 3s Rydberg transition, the near UV, $n6B^*$ band (which is relatively weak with its maximum near ~ 280 nm⁸). On the other hand, acetophenone has three near UV bands, an $n6B^*$ (320 nm), and two $B6B^*$ (280 and 230 nm).⁹ It has been well established that delocalization in unsaturated ketones alters the band positions in this manner.

The product angular distribution for acetophenone at 193 nm has been measured by Zhao et al. to be isotropic.¹³ This could be rationalized with the short lifetime we measure if it were due to intersystem crossing followed by slower dissociation from a triplet state, similar to what was found for the S_2 state.¹² However, if the short excited state lifetime is due to predissociation, then the isotropic product distribution cannot be ascribed to rotational averaging of a long-lived excited state, but may be due to overlapping transitions near 193 nm which could result in an overall nearly isotropic transition moment or the angle between the dissociating bond and the transition moment for excitation may be close to the magic angle. We have observed other instances of short-lived excited state lifetimes (<200 fs) for which the angular product distributions were found to be isotropic, such as the S_1 state of

acetone² and the 193 nm transitions for acetyl cyanide and acetic acid.³ For the S_1 state of acetone, the isotropy may arise from vibronic states with opposite transition moment directions promoting the absorption^{2,14} and for acetyl cyanide and acetic acid, the transition moment is close to the magic angle with respect to the dissociating bond.³ In these cases, the secondary products were observed to appear as soon as the parent decayed, eliminating the possibility of nondissociative decay to an intermediate state. Product signals (at masses other than the parent mass) have been detected for acetophenone, suggesting that the excited state lifetime is due to predissociation, but further studies are needed to ascertain that these are due to neutral species probe ionization rather than probe-induced dissociation of ions generated by multiphoton excitation by the pump.

The internal energy distribution has been measured for CO from photodissociation of diethyl ketone (DEK) and acetone at 193 nm.¹⁵ The amount of CO internal energy from DEK was more than expected compared to what was observed for acetone under similar assumptions for the dissociation mechanism. The conclusion was that the fragment energies were partitioned nonstatistically and that propionyl radical was farther from achieving energy redistribution, less complete IVR, than acetone. Since the primary lifetime for DEK is faster than for acetone, these results appear to be correlated. The initially excited state for DEK has a short lifetime, IVR is more restricted and this results in a nonstatistical CO internal energy for DEK. There are, however, many intervening processes, such as details of the intermediate dynamics, that probably influence the difference as well. .

Attempts to measure secondary dissociation dynamics using 390 or 260 nm probe pulses for the aliphatic ketones proved unsuccessful because the signal for product ions was dominated by dissociative ionization. Therefore, the time dependence of the signals only provided redundant information on the primary dissociation. We were able to extract acetyl dynamics for acetone photodissociation because there was less dissociative ionization using 390nm probe pulses than for the ketones investigated here. It is easier to measure secondary dissociation dynamics when the primary dissociation is rapid; in this case dissociation ionization poses less of a problem since it disappears in a short time. Example of this are the previous studies of higher Rydberg states of ketones by Kim et al^{16,17} and our results for acetyl cyanide and acetic acid.³ Acetophenone presents such an opportunity

and we are currently investigating dynamics of the intermediates in this case and plan to present the results in a future publication.

In conclusion, for excitation near 193 nm the primary dissociation dynamics for several aliphatic ketones were measured and the excited state lifetimes were resolved and determined to lie in the range 2-9 ps. The behavior is similar to what was observed for acetone and the same mechanism is invoked, predissociation from the 3s Rydberg state. The cyclic ketones were found to exhibit somewhat slower lifetimes, which is attributed to predissociation being accelerated by internal rotation in the straight chain ketone. The effect of delocalization in altering the electronic structure or rapid internal conversion of an aromatic ketone is demonstrated in the short lifetime measured for acetophenone. This result is interpreted as the presence of a valence state that is either directly excited and has a short lifetime or that induces a faster predissociation from the Rydberg state.

Acknowledgments

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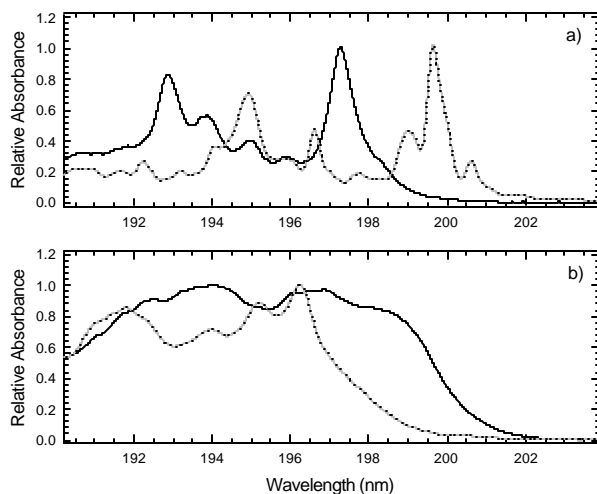
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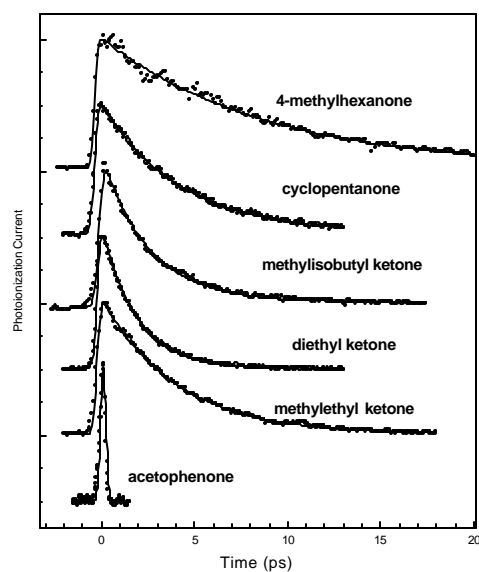
Figure Captions

1. Normalized absorption spectra measured for: a) 4-methylcyclohexanone (solid line) and cyclopentanone (dotted line); b) diethyl ketone (solid line) and methylisobutyl ketone (dotted line).



Owrutsky & Baronavski, Figure 1

2. Ultrafast photoionization curves measured for ketones. The points are the data and the solid lines are fits to single exponential decays. The decay times are listed in Table I.



Owrutsky & Baronavski, Figure 2

Table I. Excited state lifetimes for ketones near 193 nm.

Molecule	Lifetime (ps) ^a
methylethyl ketone	4.0
diethyl ketone	2.0
methyisobutyl ketone	2.6
cyclopentanone	4.1
4-methyl cyclohexanone	8.9
acetophenone	<0.2
acetone	4.7 ^b

a. Uncertainties are $\pm 10\%$.

b. Ref. 1.